

Remarks

Claims 6 - 16 are pending. Favorable reconsideration is respectfully requested.

Claims 6, 12, 15 and 16 have been rejected under 35 U.S.C. § 112 ¶2 for lack of antecedent basis for certain terms in the claims, and for improper dependency. Claims 6 and 12 have been amended to provide antecedent basis for the claim terms identified by the Office. Claims 15 and 16 have been amended to be dependent upon claim 12. Withdrawal of the rejections under 35 U.S.C. § 112 ¶2 is respectfully solicited.

The claims have been newly rejected under 35 U.S.C. § 103(a) over *Severs* U.S. Patent 3,855,280 ("*Severs*") in view of *Williams* EP 098 5657 ("*Williams*") in view of *dePoitiers et al.* U.S. 6,663,692 ("*Poitiers*"), in view of *Calcagno et al.* U.S. 3,862,216 ("*Calcagno*"), further in view of *Broz* U.S. 3,904,656 ("*Broz*"). Applicants respectfully traverse this rejection.

The subject invention is directed to an improved process for the production of vinyl acetate. Vinyl acetate is a commodity chemical used in enormous amounts throughout the world. Among its principle uses are production of vinyl acetate polymers, vinyl acetate/ethylene copolymers, and polyvinyl alcohol polymers (by hydrolysis of vinyl acetate polymers or copolymers). Processes for producing vinyl acetate have been known for a long time, well over 50 years, and the process is very technologically mature. Due to the large tonnage of vinyl acetate produced, even what appear to be very small improvements in space time yield, conservation of raw materials, energy usage, etc., are highly significant. The industry has long sought for methods to improve the economics of vinyl acetate production, which is well known to those skilled in the art, and is attested to by the varying ages of the cited references, ranging from *Severs*, filed in 1972, some 37 years ago, and *Portiers*, filed in 2001. While numerous processes have ben proposed, *Calcagno's* liquid phase process being but one example, today and for many years previous, the only commercial process for producing vinyl acetate is the gas phase process.

The aim of Applicants was to improve upon vinyl acetate production by preventing the build-up of inerts in the reactor in a cost-effective manner, thus increasing space-time yield while still allowing for recycle of unreacted ethylene, a costly reactant, from the product stream. Applicants achieved these and other objects by scrubbing the product gas stream with acetic acid at system pressure, removing vinyl acetate and forming a stream containing little or no vinyl acetate, removing CO₂ from the vinyl acetate-free gas stream, and diverting 1 to 25% of this stream to other processes which utilize ethylene, recycling the remainder to the reactor without separation of other inerts. As a result of this process, the major portion of ethylene is recycled without increasing the inerts in the reactor, and yet the expense of removing inerts from this stream is dispensed with. The ethylene not recycled is not flared or used as (an expensive) fuel, but instead is used in other ethylene-consuming processes, for example in the production of acetic acid. The process thus not only maintains a high space time yield, but is also very economical.

Severs is directed to a totally different process. *Severs* discloses vinyl acetate production in columns 1 - 7 and indicates that a rate-limiting factor in the gas phase process is the low amount of oxygen in the reactor. The oxygen content is limited by the "explosive limit" oxygen concentration. Reference may be had to numerous publications respecting explosive limits, particularly the seminal articles on this subject published by the U.S. Bureau of Mines. Typically, in a mixture of oxygen and combustible gas, the mixture is explosive over a relatively wide range of concentrations. Gas mixtures with very high oxygen content are often non-explosive, and mixtures with a very low oxygen concentration are also non-explosive. Since ethylene and oxygen are principle reactants (with acetic acid) in vinyl acetate production, it is not possible to operate at either extreme end of the "explosive" scale. The necessity for all three reactants (acetic acid, ethylene, oxygen) to be present limits oxygen concentration to 7 - 8% by volume (col. 6, lines 66 - 68). Oxygen contents above this amount causes the mixture to be explosive. This relatively low oxygen concentration, however, limits the reaction rate, and thus the space-time yield.

Severs teaches raising the oxygen concentration by diluting the reactant gases with large amounts of lower alkanes (one species of "inerts")to alter the explosive limit and thus be able to increase the oxygen concentration. The amount of added alkane is such that it typically replaces ethylene on about a 1:1 volume (and mole) basis (column 8, lines 11 - 18).

In the process described by *Severs*, vinyl acetate is separated from the product gas stream by condensing vinyl acetate from the product gas and feeding the liquid condensate and remaining gas stream to a gas/liquid separator. The gas from the separator is then scrubbed with water (column 5, lines 52 - 67). A portion of the gas stream is then purged to remove inerts, and scrubbed to remove carbon dioxide. *Severs* notes that this process results in the loss of about 5 atmospheres of pressure, and due to the size of the recycle stream, the power required to recompress the scrubbed recycle stream is substantial (col. 6, lines 13 - 24). The recycle stream typically includes 40 - 60% ethylene, 5 - 30% alkane diluent, 7 - 14% acetic acid, at least 5% oxygen, the remainder being inert gases, predominately carbon dioxide, nitrogen, argon, and water vapor. (Col. 9, lines 35 - 42).

As shown in the examples, the reactor contains a very low ethylene content due to dilution with alkane, but a higher oxygen content. Prior to dilution (conventional process), the ethylene concentration was 54% (by volume; all percents herein are volume percents, equivalent also to mol percentages), whereas in the *Severs* process, it is lowered to 44%. A large amount of inerts are also present, 26%, in both the alkane-diluted process and conventional process.

The present process differs substantially from *Severs*. First, the aim of Applicants is to reduce the concentration of inerts in the reactor, while the aim of *Severs* is to increase the concentration by purposefully adding inerts. The increased amount of inerts raises the oxygen-limited explosive limit. Second, the product stream of Applicants' process is not condensed to remove vinyl acetate, but is scrubbed with acetic acid to remove vinyl acetate. These processes are totally distinct from each other. Third, the product gas of Applicants is fed at system pressure to the acetic acid scrubber, thus not requiring large centrifugal compressors to recompress the

recycle stream. In the *Severs* process, severe depressurization occurs, requiring a huge energy burden for recompression. *Severs* does not teach or suggest the claimed process.

Williams teaches a process quite distinct from *Severs*, and incompatible therewith. These references are incapable of combination, as they teach in opposite directions.

The standard for combining references is very high. In the case of *In re Anita Dembiczak* and *Benson Zinbarg*, 50 U.S.P.Q.2d 1614 (Fed. Cir. 1999), the CAFC has indicated that the requirement for showing the teaching or motivation to combine references is "rigorous." *Dembiczak* at 1617. Moreover, this showing, which is rigorously required, must be "clear and particular." *Dembiczak* at 1617. See also, *C.R. Bard v. M3 Sys., Inc.*, 48 U.S.P.Q.2d 1225, 1232 (Fed. Cir. 1998). It is well established that merely because references can be combined, the mere suitability for logical combination does not provide motivation for the combination. See, *Berghauser v. Dann, Comr. Pats.*, 204 U.S.P.Q. 398 (DCDC 1979); *ACS Hospital Systems, Inc. v. Montefiore Hospital*, 221 U.S.P.Q. 929 (Fed. Cir. 1984). Moreover, mere conclusory statements supporting the proposed combination, standing alone are not "evidence". *McElmurry v. Arkansas Power & Light Co.*, 27 U.S.P.Q.2d 1129, 1131 (Fed. Cir. 1993). See also, *In re Lee*, 61 U.S.P.Q. 2d 1430 (Fed. Cir. 2002). It is also well established that to be combined in an obviousness rejection, the references first must be capable of physical combination. See, *e.g. In re Avery*, 186 USPQ 161 (CCPA 1975).

Here, *Severs* and *Williams* are incapable of combination both physically and legally, as they teach in opposing directions. *Williams* has been widely discussed in previous responses, these discussions incorporated herein by reference. For sake of brevity, *Williams* teaches that the amount of ethylene in the reactor be at least 60 mol percent, and teaches minimizing the inerts contained in the reactor by one or a combination of ten methods described in ¶[0028].

At this point, Applicants apologetically must correct the statement made by the Office on page 6 of the Office Action, that "of the ten methods suggested by *Williams* to reduce

the carbon dioxide and other inert gases, one discloses the use of an off-gas prescrubber prior to the carbon dioxide removal system." This is incorrect. What *Williams* states for this method is: "Reduce/minimize inerts in water used in the off-gas prescrubber prior to the carbon dioxide removal system." Moreover, this prescrubber uses water, not acetic acid.

Severs and *Williams* are uncombinable. *Severs* teaches purposefully lowering ethylene concentration by introducing alkane inert gas, preferably methane, while *Williams* teaches lowering inerts and increasing ethylene concentration above 60 mol percent. In Table 1, *Williams* includes a comparative example employing the same ethylene concentration as *Severs* (44 mol % = vol. %), and shows that a much lower space time yield as well as lower selectivity is achieved with this diluted ethylene concentration. Thus, *Williams* teaches not to do what *Severs* did, and *Severs* teaches not to do what *Williams* did. These references are uncombinable, and withdrawal of the rejection under 35 U.S.C. § 103(a) is solicited for this reason.

Furthermore, the Office states that

Williams et al. recovers the unreacted ethylene from the gases withdrawn from the reactor used for making the vinyl acetate, by membrane separation or chemical treatment. The chemical treatment process may comprise steps (i) separating the condensable products from the gases by condensation, (a') contacting the gases of step (i) with acetic acid in a scrubber to remove residual vinyl acetate product, (b') treating the product of step (a') with a water scrubber to remove acetic acid and (c') removing carbon dioxide from ethylene in the product of step (b') by using a Benfield system. (see page 4, paragraph [0028] - [0034]. The Benfield system is a carbon dioxide removal system that uses absorption.

Applicants respectfully submit that this interpretation of *Williams* is erroneous. What *Williams* states, in ¶[0033] and [0034] is:

[0033] The unreacted ethylene may be recovered from the gases withdrawn from the reactor by the steps of (i) separating condensable products from the gases by condensation and (ii) treating the gases from step (i) to recover ethylene, for example by membrane separation or chemical treatment. The condensable products may be separated from the withdrawn gases by condensation for example by using a heat exchanger or by quenching the gases by flowing counter to a flow of liquid acetic acid and/or condensable products which absorbs the vinyl acetate product.

[0034] Chemical treatment may comprise the steps of (a') contacting the gases from step (i) with acetic acid in a scrubber to remove residual vinyl acetate product, (b') treating the product of step (a') with water in a scrubber to remove acetic acid and (c') removing carbon dioxide from the ethylene in the product for step (b') by contacting with potassium carbonate. A Benfield system may be used.

The "chemical treatment" referred to by *Williams* is the chemical treatment of the gases from step (i): "treating the gases from step (i) by . . . chemical treatment." The gases of step (i) have already had vinyl acetate removed by condensation.

Thus, *Williams*, like *Severs*, teaches that first, the most substantial part of the vinyl acetate in the product stream is removed by condensation. This process involves a large loss of system pressure, about 30 - 40% of system pressure, as indicated by *Severs*. Thus, the combination of *Severs* and *Williams*, even if the references are legally combinable, teach that vinyl acetate is removed by condensation. The residual gas from the condenser is then scrubbed with acetic acid, and then with water. By contrast, Applicants do not condense vinyl acetate, with accompanying loss of system pressure, but remove vinyl acetate by scrubbing with acetic acid, at system pressure. The combination of *Severs* and *Williams* thus does not teach or suggest the claimed invention, even were these references combinable.

Severs also teaches (col. 6, lines 6 - 12), that all the gas exiting the CO₂ scrubber is recycled back to the reactor. Applicants' claims require that a portion of this gas stream not be recycled. Thus, this feature is not taught by *Severs*, nor is it taught by *Williams*.

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Portiers has been cited by the Office for allegedly providing the claimed step d), which requires directly feeding the product gas stream to a recycle gas scrubber charged with acetic acid, at system pressure. However, Applicants respectfully submit that *Portiers* contains no such teaching, or any suggestion of such a process step.

Portiers is directed to an improvement in scrubbing of carbon dioxide from a gas stream which also contains at least one of acetic acid, acetate esters, and aldehydes. The process is especially useful in the production of vinyl acetate. *Portiers* discloses vinyl acetate production with reference to Figure 1, where ethylene, oxygen, and acetic acid are fed to a gas phase reactor 1. The product stream from this reactor, however is not fed directly at system pressure to a recycle gas scrubber charged with acetic acid as required by the claims. Rather, it is fed to heat exchanger 24 and then to absorption column 2 where the gas stream is quenched at reduced pressure to condense vinyl acetate. A vinyl acetate-containing liquid product stream 10 is taken off the absorption column, and only then is the gas stream 11 fed to scrubber 3 to which demineralized water and fresh acetic acid are introduced. Note the example, where the reactor is operated at 8 bar and the absorption column (which is not a scrubber) is operated at a reduced pressure of 7 bar.

Thus, not only is the gaseous product stream not fed directly to a scrubber, it is also not maintained at system pressure. Thus, the combination of *Severs*, *Williams*, and *Portiers* does not teach or suggest the claimed invention. Factually, the process of *Portiers*' is very similar to the individual processes of *Severs* and *Williams*. In all these processes, the product gas stream from the reactor is first cooled and condensed to separate a liquid vinyl acetate product stream at reduced pressure. Following the condensation, the gas stream is treated to remove liquid impurities by scrubbing with acetic acid/water prior to scrubbing with potassium carbonate to remove CO₂. That is not the process of Applicants. In Applicants' process cooling and condensation to form a liquid vinyl acetate stream is not practiced at all, nor is a vinyl acetate/aldehyde/acetate ester-containing gas stream subsequently scrubbed. Instead, Applicants scrub the product gas stream at system pressure with acetic acid, which immediately removes vinyl acetate and other condensable fractions, avoiding the expense of a heat exchanger or

condenser. Note in *Portiers*, for example, that while the reactor is operated at 160°C, the absorption column temperature is only 30 - 40°C. This well over one hundred degree temperature difference represents a huge energy loss. Moreover, because the absorption column of *Portiers* is operated at reduced pressure and the pressure is still further reduced by subsequent scrubbing, CO₂ removal, and venting of a portion of the product stream, considerable energy must be expended to repressurize the recovered ethylene.

In Applicants' process, very surprisingly, the combination of vinyl acetate removal by acetic acid scrubbing followed by CO₂ removal also reduces the amounts of inerts in the gas stream. Note page 5 of the application, where the gaseous inerts leaving the reactor totaled maximally 17 volume percent. Following CO₂ absorption, despite a significant reduction in CO₂ concentration (12 - 18% down to 1 - 4%), which would be expected to increase the volume percentages of ethylene and the inerts (since these will then constitute a greater part of the CO₂-depleted gas¹), instead, the concentration of inerts is reduced to a maximum of only 9.4%, approximately a 50% reduction. In particular, the amounts of ethane and methane are reduced to about half their concentration. The ethylene concentration is increased. As a result, a greater portion of the gas stream exiting the CO₂ scrubber can be recycled, without any expensive inerts-removal step being required for this gas stream, and without inerts building up in the reactor. The ethylene gas stream exiting the scrubber is pure enough to be useful in other processes employing ethylene, such that the portion not recycled is still put to good, economical use. None of *Severs*, *Williams*, or *Portiers* teaches treating the product gas stream in such a way that inerts are lowered substantially without the use of inerts-removing methods such as membrane separators.

Calcagno is a very different reference not believed relevant to the claimed invention. The *Calcagno* process is a very old and antiquated liquid phase process for producing vinyl acetate, to which no one skilled in the art would look to for any purpose. Note that the ethylene to vinyl acetate selectivity in the *Calcagno* process is only 80%, and only 2 mol% of

¹For illustration, if all CO₂ is removed from a mixture of 33% oxygen, 33% ethylene, and 33% CO₂, the volume percents of the remaining gases will be 50% CO₂ and 50% ethylene.

ethylene is converted on each pass through the reactor. *Calcagno* directs a portion of the gaseous product stream, from which liquids have been separated, but from which CO₂ and inerts have not been removed, into a separate column where ethylene is oxidized to acetic acid and not more than 20% byproducts. Some 13% of the gas from the acetic acid reactor, predominately ethylene, carbon dioxide, and inerts, is discharged or flared, representing a considerable waste of valuable ethylene feedstock.

Thus, *Calcagno* does teach use of a portion of the ethylene recycle stream not recycled to his liquid phase process. However, *Calcagno* does not supply any of the deficiencies of *Severs*, *Williams* or *Portiers*, and thus the combination of these four references still does not teach or suggest the claimed invention.

The improved yield and selectivity of Applicants' process should also be noted. The lowest selectivity (Example 1) was 91.5%, while the highest was 93%, all higher than the selectivities achieved by *Williams*, who takes great pains to remove inerts. Because Applicants do not employ a separate, inerts-removal step, their process is simpler and more economical. It is particularly surprising that an increased selectivity could be achieved despite the fact that inerts remain in the cycle gas. The increased selectivity is very important commercially. Even a 0.1 or 0.05% increase in selectivity is hugely important for high volume commodity products.

Withdrawal of all rejections of record is respectfully solicited.

Applicants submit that the claims are now in condition for Allowance, and respectfully request a Notice to that effect. If the Examiner believes that further discussion will advance the prosecution of the Application, the Examiner is highly encouraged to telephone Applicants' attorney at the number given below.

S/N: 10/599,880
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Atty Dkt No. WAS 0813 PUSA

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Respectfully submitted,

Willibald Dafinger et al.

By



William G. Conger
Reg. No. 31,209
Attorney/Agent for Applicant

Date: March 5, 2009

BROOKS KUSHMAN P.C.
1000 Town Center, 22nd Floor
Southfield, MI 48075-1238
Phone: 248-358-4400
Fax: 248-358-3351